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Form Approved  
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1. REPORT DATE (DD-MM-YYYY)

2. REPORT TYPE

Technical Papers

3. DATES COVERED (From - To)

4. TITLE AND SUBTITLE

5a. CONTRACT NUMBER

N/A

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)

5d. PROJECT NUMBER

2308

5e. TASK NUMBER

M19B

5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

Air Force Research Laboratory (AFMC)  
AFRL/PRS  
5 Pollux Drive  
Edwards AFB CA 93524-7048

8. PERFORMING ORGANIZATION  
REPORT

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)

Air Force Research Laboratory (AFMC)  
AFRL/PRS  
5 Pollux Drive  
Edwards AFB CA 93524-7048

10. SPONSOR/MONITOR'S  
ACRONYM(S)

11. SPONSOR/MONITOR'S  
NUMBER(S)

12. DISTRIBUTION / AVAILABILITY STATEMENT

Approved for public release; distribution unlimited.

20030103 055

13. SUPPLEMENTARY NOTES

14. ABSTRACT

15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:

a. REPORT

Unclassified

b. ABSTRACT

Unclassified

c. THIS PAGE

Unclassified

17. LIMITATION  
OF ABSTRACT

A

18. NUMBER  
OF PAGES

19a. NAME OF RESPONSIBLE  
PERSON

Leilani Richardson

19b. TELEPHONE NUMBER

(include area code)

(661) 275-5015

Standard Form 298 (Rev. 8-98)  
Prescribed by ANSI Std. Z39.18

21 separate items enclosed

2308/198

TP-1998-083

MEMORANDUM FOR IN-HOUSE PUBLICATIONS

FROM: PROI (TI) (STINFO)

5 May 98

SUBJECT: Authorization for Release of Technical Information, Control Number: AFRL-PR-ED-TP-1998-083  
**J.J. Schwab, J.D. Lichtenhan et al.** "Polyhedral Oligomeric Silsesquioxanes (POSS): Silicon Based Monomers and Their Use in the Preparation of Hybrid Polyurethanes"  
(Statement A)

# POLYHEDRAL OLIGOMERIC SILSESQUIOXANES (POSS): SILICON BASED MONOMERS AND THEIR USE IN THE PREPARATION OF HYBRID POLYURETHANES

*Joseph J. Schwab<sup>†</sup>; Joseph D Lichtenhan<sup>‡</sup>; Kevin P. Chaffee<sup>‡</sup>; Patrick T. Mather<sup>§</sup>; Angel Romo-Uribe<sup>§</sup>*

*<sup>†</sup>Raytheon STX, Air Force Research Laboratory, Edwards AFB, CA 93524. <sup>‡</sup> Air Force Research Laboratory, Edwards AFB, CA 93524. <sup>§</sup> Air Force Research Laboratory, Wright-Patterson AFB, OH 45433.*

## Abstract

A series of Polyhedral Oligomeric Silsesquioxane (POSS) monomers bearing reactive hydroxyl functionalities, suitable for incorporation into step-growth polymers, is described. These monomers are difunctional in nature and are particularly well suited for use as chain extenders in the synthesis of polyurethanes. This work describes the synthesis of these POSS and their incorporation into a series of polyurethanes. Preliminary thermal, mechanical and rheological data for the POSS containing polyurethanes will also be discussed.

## Introduction

Although there is very little doubt that during the past 40 years there has been a prodigious effort put forth by both industry and academia towards the synthesis of new monomeric feedstocks for the polymer industry, almost all of this effort has been expended in the pursuit of entirely organic materials. Furthermore, despite this great expenditure of effort and resources the fact still remains that the last great development in the field of polymer chemistry occurred in approximately 1955 with the development of arene monomer feedstocks and the subsequent incorporation of these rigid segments into the polymer backbone, to give rise to today's high performance polymers. However, since this discovery there has not been a similar development to compare with this breakthrough.

The rise of the inorganic and the hybrid inorganic/organic polymer field has been in part, an attempt to generate a revolutionary breakthrough rivaling the introduction of arene monomers into polymer backbones.<sup>1</sup> However, despite some success, the development of a radically new non-organic monomer feedstock technology which can be used with existing organic polymer systems has not, until recently, been forthcoming. Our approach to inorganic/organic hybrid materials involves the synthesis of discrete, well defined nanoscale hybrid reagents which can be incorporated into traditional, thermoplastic and thermoset polymer systems. The hybrid nanoscale reagents developed in our laboratory are based on polyhedral oligomeric silsesquioxane (POSS) precursors.<sup>2</sup> POSS precursors are structurally well-defined compounds composed of a silicon-oxygen framework having the general formula  $(\text{RSiO}_{3/2})_n$ , and can be easily functionalized with a wide variety of organic groups that are commonly employed in polymerization or grafting reactions. Furthermore, unlike conventional filled polymers the hybrid polymers prepared from POSS reagents are unique in that the inorganic portion of the hybrid is covalently linked to the organic polymer chain. Thus, POSS technology represents a radical departure from traditional polymer technology in that it exploits new material composition and the new materials science concept of tailorable, nanostructural control of physical properties.

Segmented thermoplastic polyurethane elastomers represent one of the most versatile groups of engineering thermoplastics having elastomeric properties. The highly desirable mechanical and thermophysical properties of these materials is known to arise from a microphase separation caused by the thermodynamic incompatibility or immiscibility of hard segments and soft segments.<sup>3</sup> In typical polyurethanes, hard segments which consist of urethane linkages form distinct domains which are held together by noncovalent van der Waals and hydrogen bonding forces. Upon heating, these weak binding forces are lost and a breakdown of the hard segment domains occurs, resulting in a loss of the polymer's physical properties. Although the effects from the incorporation of a covalently bonded POSS hybrid nanocomposite structure on the microphase separation of hard segments in linear segmented polyurethanes cannot be predicted, it is hoped that potentially strong interchain interactions due to the incorporation of POSS into the hard segments might result in substantially stronger, reinforced hard segment domains and thus give rise to greater thermal stability in the POSS polyurethanes.

Here we describe our initial results in preparing POSS monomers suitable for use in step growth polymerizations and their use in the synthesis of thermoplastic polyurethanes.

## Experiment

### Materials

2,2'-Diallylbisphenol A was obtained from Ciba-Geigy Corporation and used as received. Polytetramethyleneglycol (PTMG, MW = 2000) was obtained from BASF corporation and used as received. Platinum divinyl complex (2-3% platinum) in xylenes was purchased from United Chemical Technologies and used as received. Trimethylolpropane allyl ether, 4,4'-methylenebis(phenyl isocyanate) (MDI) and dibutyltin dilaurate (DBTDL) were purchased from Aldrich Chemical Company and used as received. Hexamethylene diisocyanate was distilled prior to use. Triethylamine and tetrahydrofuran (THF) were dried over oil dispersed sodium metal and either distilled or vacuum transferred prior to use. The synthesis of  $(c\text{-C}_6\text{H}_{11})_7\text{Si}_8\text{OSi}(\text{CH}_3)_2\text{H}$  is described elsewhere.<sup>4</sup> Hydrogenation of diallylbisphenol A and trimethylolpropane allyl ether was carried out in ethyl acetate using 10% Pd on carbon.

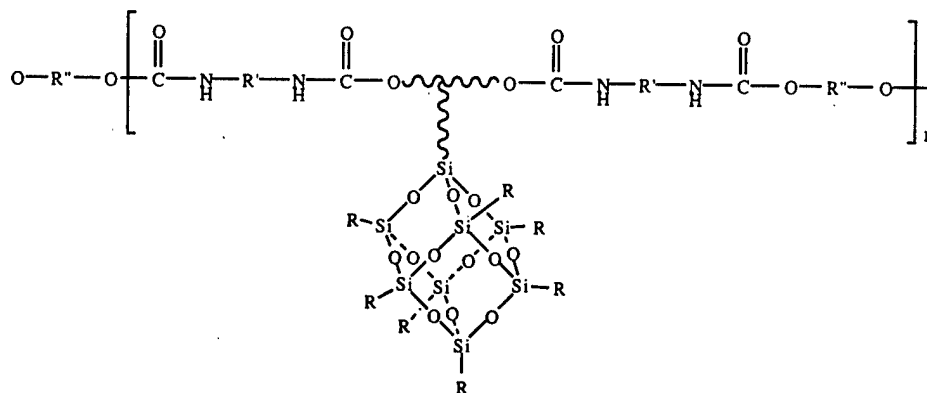
### POSS Monomers

In a typical procedure, a solution of platinum catalyst (1 drop) in xylenes was added to a solution of  $(c\text{-C}_6\text{H}_{11})_7\text{Si}_8\text{OSi}(\text{CH}_3)_2\text{H}$  and trimethylolpropane allyl ether (2eq) in toluene. The reaction mixture was stirred for 18 h at room temperature, after which activated carbon was added to the reaction mixture. The solution was filtered through celite, the volume of solvent reduced and the product precipitated with acetonitrile. The product was collected by vacuum filtration and dried. Purity was checked by HPLC and NMR spectroscopy and found to be greater than 98%.

For POSS bisphenol A monomers containing two POSS cages a 1:1 reaction mixture of  $(c\text{-C}_6\text{H}_{11})_7\text{Si}_8\text{OSi}(\text{CH}_3)_2\text{H}$  to 2,2'-diallylbisphenol A was used, while for POSS bisphenol A monomers containing only a single cage a 1:4 reaction mixture of  $(c\text{-C}_6\text{H}_{11})_7\text{Si}_8\text{OSi}(\text{CH}_3)_2\text{H}$  to 2,2'-diallylbisphenol A was used.

### Results

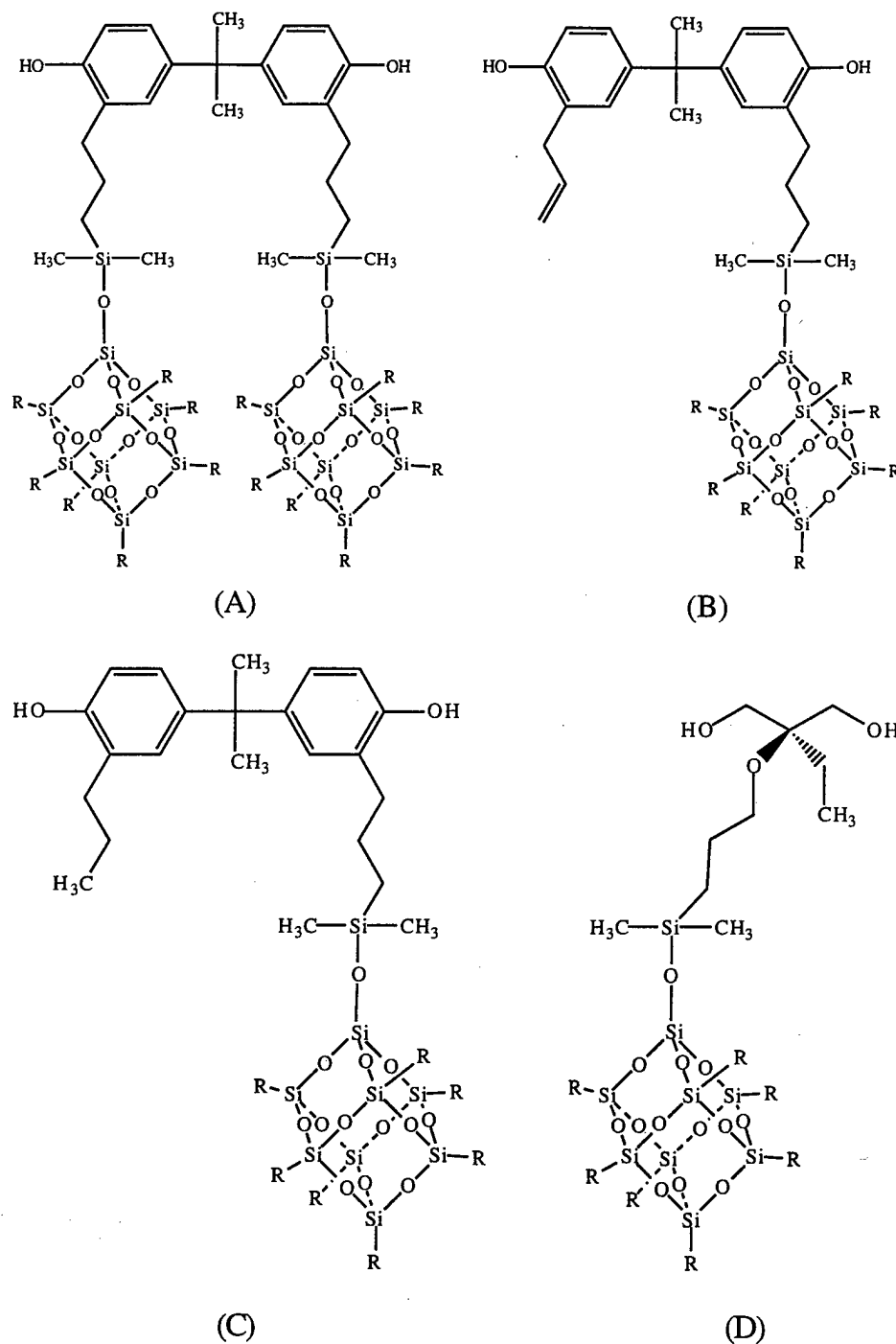
Linear, segmented thermoplastic polyurethanes are typically prepared from the reaction of three basic components; a difunctional isocyanate, a long chain, diol terminated polyester or polyether and a short chain diol (chain extender). The approach taken in this work for the synthesis of POSS hybrid polyurethanes focuses on the use of POSS diols as chain extenders in the synthesis polyurethanes. (Figure 1.). In this way, incorporation of the POSS framework directly into the hard segment of the polyurethane backbone is guaranteed.



**Figure 1.** Schematic representation of POSS hybrid polyurethanes.  $\text{R} = c\text{-C}_6\text{H}_{11}$  or  $c\text{-C}_5\text{H}_9$ .  $\text{R}'$  diisocyanate.  $\text{R}''$  = polyetherdiol.

Two different types of POSS diols suitable for use as chain extenders in polyurethanes have been prepared. Originally, POSS functionalized bisphenol A monomers were prepared for the synthesis of nanostructured POSS-BMI resins<sup>5</sup>, however, a significant body of work detailing both the use as well as the physical properties of polyurethanes having bisphenol A chain extenders<sup>6</sup> prompted us to use these monomers for the synthesis of POSS hybrid urethanes. Starting from 2,2'-diallylbisphenol A monomers having either one or two POSS frameworks can

be synthesized. Furthermore, mono-POSS bisphenol A monomers having both saturated and unsaturated side chains are also readily prepared. The ability to prepare mono- and difunctional POSS bisphenol A monomers is useful in that it allows for easy control of the POSS content in the urethane polymer, while the presence of unsaturated side chains can be used to crosslink polymer chains.



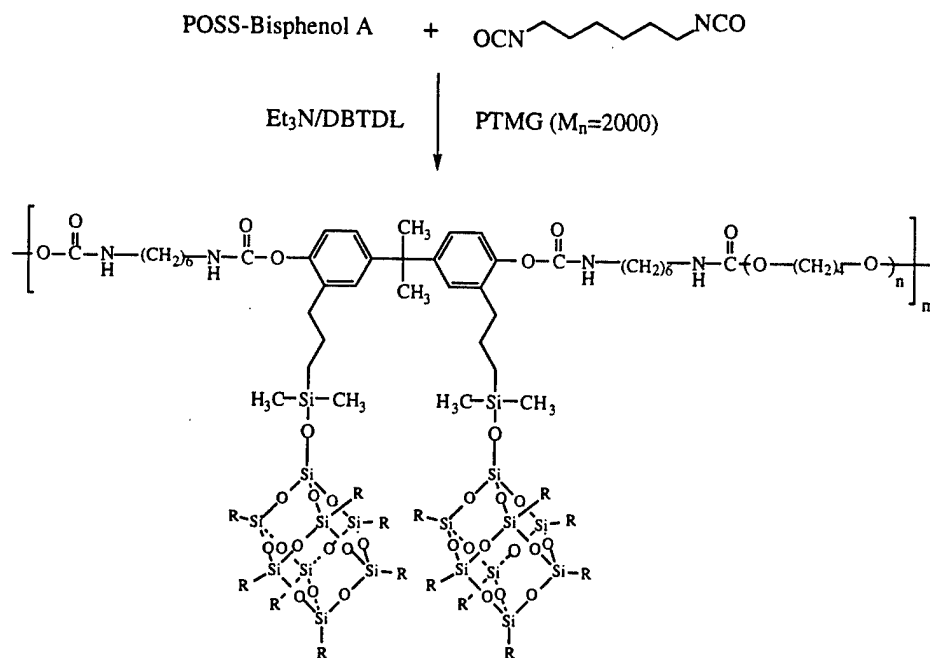
**Figure 2.** Examples of POSS diol monomers based on bisphenol A (A, B and C) and trimethylolpropane (D).  $R = \textit{c}\text{-C}_6\text{H}_{11}$  or  $\textit{c}\text{-C}_5\text{H}_9$ .

Although the use of bisphenol A type chain extenders in the synthesis of polyurethanes is well documented,<sup>6</sup> it is also known that the use of phenols in the synthesis urethanes results in a urethane linkage which is thermally unstable, and will revert back to the original phenol and

isocyanate at elevated temperatures (i.e. blocked isocyanates). Therefore, a second class of POSS diols based on trimethylolpropane were also prepared. These monomers more closely resemble the aliphatic diols used as chain extenders in the synthesis of polyurethanes. These monomers are readily prepared via the hydrosilation of  $(c\text{-C}_6\text{H}_{11})_7\text{Si}_8\text{O}_{12}\text{OSi}(\text{CH}_3)_2\text{H}$  to either 2,2'-diallylbisphenol A or trimethylolpropane allyl ether. Examples of several POSS diols are shown in Figure 2.

Two types of processes, the prepolymer method and the one-shot method, can be used for the synthesis of polyurethanes. In the prepolymer method, a long chain diol is allowed to react with an excess of diisocyanate to form a low molecular weight isocyanate terminated "prepolymer", which in turn is allowed to react with a short chain diol (chain extender) to produce a high molecular weight urethane polymer. In the one shot method the three components of the polyurethane are mixed together and allowed to react all at once in the melt phase. In the current work, polyurethanes were prepared using each of these protocols.

For the synthesis of POSS hybrid polyurethane a variation of the prepolymer method was used. In a typical synthesis, a THF solution of POSS diol was allowed to react with two equivalents of hexamethylenediisocyanate in the presence of a catalytic amount of dibutyltindilaurate(DBTDL)/triethylamine (1:1). After 18 h a THF solution of polytetramethylene glycol (PTMG) (MW = 2000) in THF was added and the reaction mixture stirred for an additional 18 h. During this time a noticeable increase in the viscosity of the reaction mixture was observed. The POSS-urethane copolymer was isolated by addition of the THF solution to a large excess of methanol followed by filtration of the precipitated polymer. Polyurethanes containing no POSS monomer were prepared under identical conditions. Figure 3 shows a typical synthetic scheme for one such hybrid urethane.



**Figure 3.** Typical synthesis of a POSS hybrid polyurethane.  $R = c\text{-C}_6\text{H}_{11}$  or  $c\text{-C}_5\text{H}_9$ .

For the synthesis of hybrid POSS polyurethanes via the one shot method, a twin screw micro-scale batch mixer which allows for indefinite recirculation of material was used. In a typical synthesis, PTMG, diisocyanate and chain extender were combined in the mixer at 80 °C. The temperature was ramped to 190 °C and the components allowed to react for an additional 50 min. at this temperature. The resulting polymer is extruded and cooled.

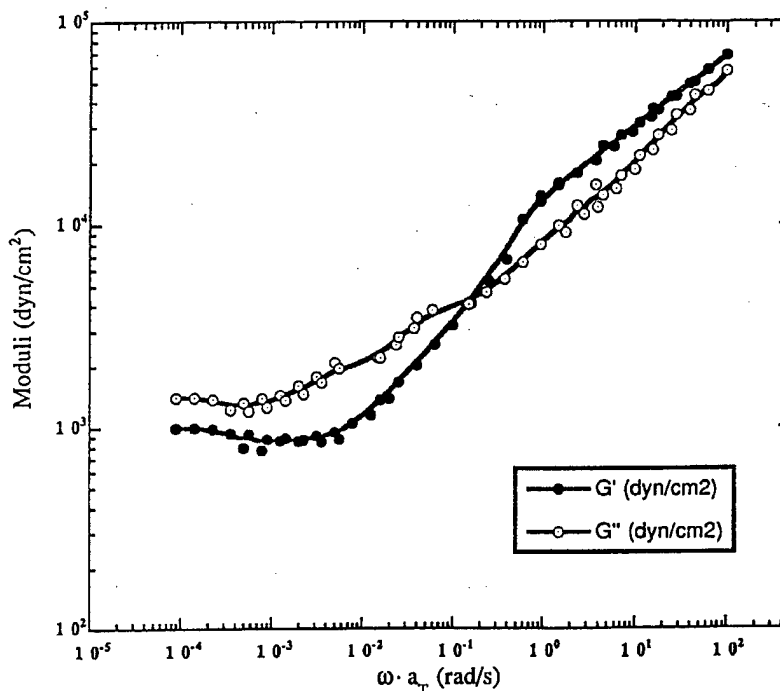
Table I shows some typical data for the POSS-polyurethane copolymers prepared using the prepolymer method. In all cases the POSS polyurethane copolymers were solid rubbers while the non POSS polyurethanes are viscous fluids. As in other POSS polymers increases in  $T_g$  are observed, as well as increases in decomposition temperature and char yields of the polymers.

**Table I.** Physical characteristics and appearance of some polyurethanes.

Polymer	Melt Transition °C	T <sub>dec</sub> *	Char Yield%	Appearance
0% POSS *	-49, 22	274°C	1.4	Viscous Fluid
29% POSS *	201	372 °C	16	Solid Rubber
43% POSS *	260, 320	344°C	20	Solid Rubber

\* Wt % POSS    \*TGA, 10% weight loss at 10°C/min heating rate

The rheological properties for the POSS-urethane containing 43 wt% POSS is shown in Figure 4. The plot shows the shear storage modulus  $G'$  and the shear loss modulus  $G''$  as a function of the oscillation frequency. The presence of a plateau region clearly shows the elastomeric nature of this system. This property is believed to result from intermolecular POSS-POSS interactions. The exact nature of these interactions is currently under investigation with both steric and associative interactions being of primary consideration. It is also worthy to note that similar reinforcing properties have been observed in other thermoplastic POSS-copolymer systems (i.e. POSS styrene systems).



**Figure 4.** Mechanical Spectrum showing thermoplastic elastomeric behavior of a POSS polyurethane with 43 wt% POSS.

Preliminary mechanical studies have been carried out on POSS polyurethanes having various weight percentages of POSS monomer. POSS polyurethanes with 17-21 wt% POSS incorporation show a 10-fold increase in modulus over the polyurethanes having no POSS incorporation. Increasing the POSS content to 34-36 wt% results in only 2.5-fold increase in the modulus relative to the 17-21 wt% polymers. Although all of the POSS polyurethanes prepared thus far have an elongation to break of greater than 400 %, the ultimate elongation to break has not yet been determined. Hardness data (Shore A) on the POSS polyurethanes prepared to date indicates that the incorporation of POSS results in a more than two-fold increase in the hardness of

the urethane polymers. However, unlike the modulus data it is not clear that increasing the wt% of POSS from 17-21 wt% to 34-36 wt% gives a corresponding increase in the hardness.

The *in-situ* structure and morphology changes during deformation of the POSS polyurethanes were also carried out by simultaneous SAXS (small angle X-ray scattering) and WAXD (wide angle X-ray diffraction) (SWAXS) techniques using synchrotron radiation.<sup>7</sup> In this technique, POSS polyurethanes strained to 400% showed an increase in orientation and arrangement of the segregated domains (hard segments), however, the dimensions of these domains appeared to be unchanged. This is in contrast to conventional polyurethanes where, destruction of the hard segment domains is observed when strains approach 400%. This result suggests that the hard segment domains of POSS polyurethanes are reinforced by the incorporation of POSS monomers into the hard segments. Furthermore, strain induced crystallization of the PTMG soft segments in POSS polyurethanes was also observed, however, unlike conventional polyurethanes in which these crystalline domains melt upon strain relaxation, melting of these domains in the POSS polyurethanes was not observed even upon complete relaxation, suggesting that these crystalline domains might also be stabilized by the reinforced hard domains.

Although we are only now beginning to develop an understanding of the effects that POSS frameworks have on polymer microstructure and the resulting effects on macroscopic properties, we believe that the observed property enhancements arise in part from the ability of the POSS segments to dominate polymer chain motions. Compared to traditional organic monomers, POSS-monomers are physically very large. Given that POSS monomers are physically large (for example, the area swept out by an octomeric POSS-monomer containing cyclohexyl substituents is approximately 15 Å, with an inner Si-Si diameter of 5.4 Å, and formula weights of greater than 1000 amu) with respect to typical polymer dimensions (5-50 Å for amorphous segments) it is conceivable that POSS monomers could dominate local chain motion. In addition, POSS frameworks may function to provide localized structure to chain segments, thereby reinforcing the polymer chains on a molecular level.

## Conclusion

A series of aromatic and aliphatic diols containing Polyhedral Oligomeric Silsesquioxanes (POSS) frameworks has been prepared. The use of these nanostructured hybrid diols and phenols as chain extenders in the synthesis of polyurethanes has been successfully demonstrated. The POSS-polyurethanes prepared using these reagents demonstrate increased modulus, hardness,  $T_g$ ,  $T_{dec}$  and increased char yields relative to the non-POSS polyurethanes. In particular, the POSS-polyurethanes exhibit increased  $T_g$  and  $T_{dec}$  as well as increased char yields. Furthermore, simultaneous SAXS and WAXD (SWAXS) have provided the first evidence that the POSS monomers do in fact provide a nanoscale reinforcement the hard segment domains.

## Acknowledgment

We thank the Air Force Office of Scientific Research, Directorate of Chemistry and Life Sciences, and the Phillips Laboratory, Propulsion Directorate for financial support.

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